III.A.16 SOFC Glass-Ceramic Seal Development at PNNL

Objectives

- Develop cost effective seals for SOFC stacks that offer low leak rates and desired reliability during long-term isothermal and thermal cyclic operation.
- Develop a scientific understanding of the degradation processes affecting performance and integrity of seals, including intrinsic materials degradation in SOFC environment and interactions with adjacent SOFC components.

Accomplishments

- Synthesized and characterized new "refractory" sealing glass compositions.
- Fabricated sealed joints for leak testing (anode-supported electrolyte/glass/ferritic stainless steel).
- Performed leak tests on joined coupons followed by microstructural characterization.
- Identified promising glass seal compositions with improved coefficient of thermal expansion (CTE) match and reduced interfacial reactivity for further evaluation and testing.

Introduction

Planar SOFC stacks require adequate seals between the interconnect and cells in order to prevent mixing of the oxidant and fuel gases, and to prevent leaking of gases from the stack. In addition, the seals must also allow the stack to be thermally cycled repeatedly (between ambient conditions and the operating temperature). Several different approaches to sealing SOFC stacks are available, including rigid, bonded seals (e.g., glass-ceramics), compliant seals (e.g., viscous glass), and compressive seals (e.g., mica-based composites). Rigid seals typically soften and flow slightly during stack fabrication (at a temperature above the operating temperature) but then become rigid (to avoid excessive flow or creep) when cooled to the operating temperature. The thermal expansion of rigid seals must be closely matched to the other stack components in order to avoid damaging the stack during thermal cycling. Compliant seals attempt to simultaneously perform the sealing function and prevent thermal stress generation between adjacent components. Compressive seals typically utilize materials such as sheet-structure silicates that do not bond adjacent SOFC components; instead, the sealing material acts as a gasket and gas-tightness is achieved by applying a compressive force to the stack.

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Approach

Candidate glass-ceramic sealing compositions were prepared by melting and casting of appropriate oxide constituents. Structural, thermal, and mechanical properties were evaluated utilizing x-ray diffraction, scanning electron microscopy (SEM), energy dispersive x-ray spectroscopy, dilatometry, and optical microscopy. Seal quality of joined interconnect/anode-supported electrolyte coupons was evaluated through room temperature leak testing following isothermal and/or thermal cycling heat treatment.

Results

The main emphasis of glass seal development work at PNNL is to identify, synthesize, characterize, and validate sealing glass formulations (glass-ceramics) with desired thermal, mechanical, electrical, and chemical properties for long-term SOFC applications. The current approach is based on a "refractory" sealing glass-ceramic concept. The refractory sealing glasses are designed to have a higher sealing temperature (e.g., 900-1,050°C), compared to a state-of-the-art glass (e.g., G18, a Ba-Ca-Al-B silicate glass) which typically seals at $\leq$850°C for operation at ~750°C. The potential advantages of refractory sealing glasses are long-term thermal stability (particularly coefficient of thermal expansion, CTE), minimal interfacial reaction with metallic interconnects, and stronger bonding at cell/interconnect interfaces due to a higher stack fabrication temperature. The glass system under investigation is similar to G18 but contains a different primary glass modifier, i.e., Sr instead of Ba. Three glass systems were evaluated:

1. YS series: Sr-Ca-Al-Y-B-Si
2. YSO series: Sr-Ca-Y-B-Si
3. YSP series: Sr-M-Y-B-Si (M=Mg, Ca, Sr, Ba)

The first glass series investigated was the YS series based on Sr-Ca-Al-Y-B-Si. In order to increase the sealing temperature, the glass composition was tailored by varying the B_2O_3 content from 9.5 to 3.5 mole% in seven glasses, and the lower bound of B_2O_3 content for forming a homogeneous glass was established. These glasses did appear to be more refractory, as evidenced by their higher softening points (for example, see the dilatometric plots for glass G18 (Figure 1) and for glass YS-1 (Figure 2) after short-term crystallization). Hermetic sealing was obtained for anode-supported electrolyte/ferritic stainless steel joins in the as-sealed condition and was maintained after 10 thermal cycles in air, or 10 thermal cycles in a reducing environment. However, the YS glasses had a lower CTE than G18, and also, like G18, exhibited a trend of decreasing CTE after aging for 1,000 h and 2,000 h. The decrease in CTE was likely due to the formation of a low CTE celsian phase similar to the $BaAl_2Si_2O_8$ formed in G18 glass.

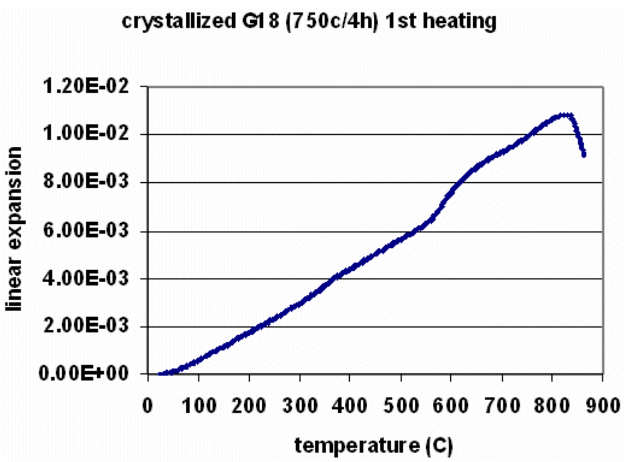

FIGURE 1. Linear Thermal Expansion of G18 Sealing Glass after Short-Term Crystallization in Air (850°C for 1 hour followed by 750°C for 4 hours)

The second glass series (YSO series) was developed by removing Al_2O_3 from the YS series; eight glasses were batched with varying SrO (42.5% to 47.5%), varying B_2O_3 (7.5% to 9.5%), varying Y_2O_3 (6% to 10%) content, and/or La_2O_3 (6%). Adding La_2O_3 to 6% or Y_2O_3 to 10% resulted in poor glass-forming behavior, i.e, bulk crystallization during the glass making process. The other glasses typically had a softening point >720°C and the CTE appeared stable over 1,000 h or 2,000 h aging with values ~11.5×10^{-6}/°C. Glass YSO-1 was selected for further investigation of sealing properties and interfacial microstructure development. Results from SEM analysis showed undesirable $SrCrO_4$ formation along the glass/metal interface for samples sealed at lower temperatures (900-950°C, see Figure 3). At higher sealing temperatures (1,000-1,050°C), however, no chromates were found, as shown in Figure 4. Thermodynamic calculations indicated that formation of chromates is favorable for Ba- or Sr-containing glasses if oxygen is available, but such reaction was apparently avoided when oxygen was excluded from the interfacial region by rapid densification of the glass at the higher sealing temperatures. The CTEs of both chromates phases were also experimentally determined and were found to be undesirably high (~21-22 $\times 10^{-6}$/°C), indicating that a protective layer may be required to minimize the formation of these interfacial phases. Both in-house developed $(Mn,Co)_3O_4$ spinel coatings and commercial Al_2O_3 coatings are under investigation. Concerning electrolyte/glass interfaces, the refractory sealing glasses exhibited improved chemical compatibility compared to G18, as no interfacial reaction phases were observed.

The final glass series (YSP) involved partial substitution of Sr with Mg, Ca, and Ba; several glasses

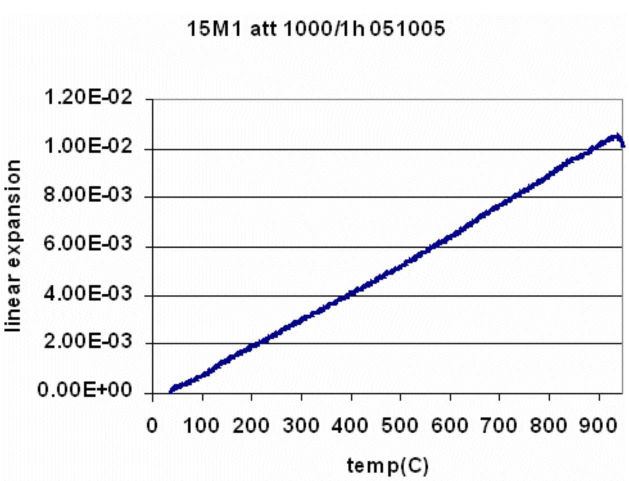

FIGURE 2. Linear Thermal Expansion of YS-1 Sealing Glass after Short-Term Crystallization in Air (850°C for 1 hour followed by 750°C for 4 hours)

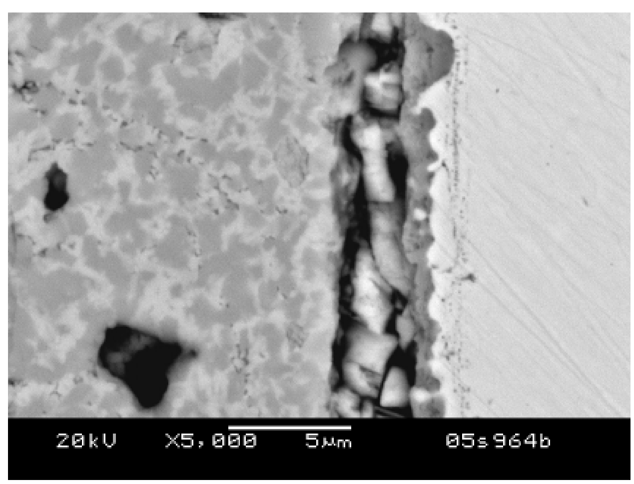

FIGURE 3. Interfacial microstructure of glass (YSO-1) at the glass/metal (Crofer22APU) interface. Sealed at 950°C/2 h in air. Note undesirable formation of $SrCrO_4$ near the interface (arrow).

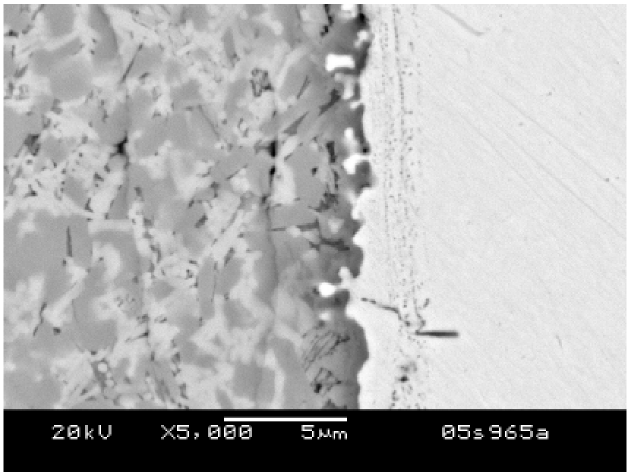

FIGURE 4. Interfacial microstructure of glass (YSO-1) at the glass/metal (Crofer22APU) interface. Sealed at 1,000°C/2 h in air. No chromate formation was observed for the higher sealing temperature, likely due to exclusion of oxygen from the interface.

were identified with CTE in the ~12.3×10^{-6}/°C range. However, again it was apparent that the issue of chromate formation must be addressed. Candidate sealing glasses were also tested in dual environments; some YSO series glasses survived four deep thermal cycles and aging up to 1,000 h at 850°C.

Conclusions and Future Directions

- Refractory glass seals have been developed, which offer excellent, stable CTE matching to other SOFC stack components. Hermetic seals have been obtained which survived isothermal and thermal cycle heat treatments. These compositions also exhibit improved interfacial stability compared to other SOFC sealing glasses, although further interfacial optimization (such as interconnect coatings) may be required to mitigate formation of undesirable, high CTE phases.
- Future work will focus on continued optimization of refractory glass seal compositions as well as larger scale testing (e.g., 4.5 inch x 4.5 inch), including isothermal and thermal cycle tests in dual environments (e.g., air/70% H_2-30% H_2O).

FY 2006 Publications/Presentations

Publications

1. Y.S. Chou, J.W. Stevenson, and P. Singh, "Thermal Cycle Stability of a Novel Glass-Mica Composite Seal for Solid Oxide Fuel Cells: Effect of Glass Volume Fraction and Stresses," J. Power Sources, 152, 168 (2005).

2. Y.-S. Chou, J.W. Stevenson, and P. Singh, "Glass Mica Composite Seals for Solid Oxide Fuel Cells," 29th International Conference on Advanced Ceramics and Composites - Advances in Solid Oxide Fuel Cells (Ceramic Engineering and Science Proceedings, Volume 26, Issue 4), p. 257 (2005).

3. Y.-S. Chou, J.W. Stevenson, and P. Singh, "Combined Ageing and Thermal Cycling of Compressive Mica Seals for Solid Oxide Fuel Cells," in Proc. 29th International Conference on Advanced Ceramics and Composites - Advances in Solid Oxide Fuel Cells (Ceramic Engineering and Science Proceedings, Volume 26, Issue 4), p. 265 (2005).

Presentations

1. "Effect of Sealing Temperature on the Interfacial Reactions of a SOFC Sealing Glass with a Metallic Interconnect Material," Y. Chou, J.W. Stevenson, and P. Singh, 30th International Conference & Exposition on Advanced Ceramics and Composites, Cocoa Beach, FL, January 22-27, 2006.

2. "Effect of Ageing on the Thermal Properties of a Novel SOFC Sealing Glass," Y. Chou, J.W. Stevenson, and P. Singh, 30th International Conference & Exposition on Advanced Ceramics and Composites, Cocoa Beach, FL, January 22-27, 2006.

3. "SOFC Interconnect and Compressive Seal Development at PNNL," Y.S. Chou, Z. Yang, G. Maupin, S. Simner, P. Singh, J.W. Stevenson, and G. Xia, 2005 Fuel Cell Seminar, Palm Springs, CA, November 14-18, 2005.